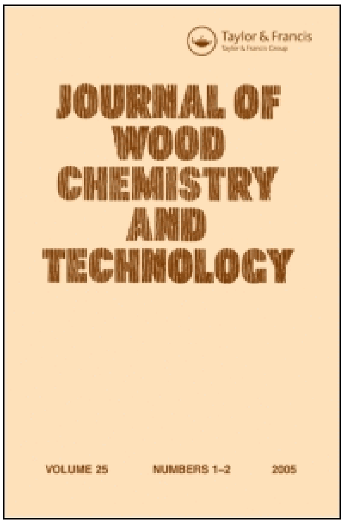

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Comparative Study of Wood Samples of the Northern Area of Catalonia by FTIR

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Abstract: The lignin and holocellulose of thirty different woods from the northern area of Catalonia (Spain) were analyzed in detail by FTIR spectroscopy. Five lignin bands and three holocellulose bands were used to characterize differences between the woods. The location and relative intensities of these components could be used to differentiate between hardwoods and softwoods. It was also shown that the lignin and amount of crystallized cellulose I was different for each type of wood.

Keywords: FTIR, lignin, holocellulose, hardwood, softwood

INTRODUCTION

Wood is an abundant, renewable, and biodegradable composite with many useful applications, such as paper pulp production, building and furniture, natural reinforcement in polymer composites, and as an important source of energy.

Based on their structural aspects, woods can be classified into two groups: angiosperms (hardwoods) and gymnosperms (softwoods). These groups differ in some properties: chemical composition, holocellulose (cellulose and hemicellulose) content, lignin content, and fiber dimensions. Softwood lignin is composed essentially of guaiacyl units, whereas hardwoods have lignin with both guaiacyl and syringyl units. However, the cellulose component is very similar in all trees and consists mainly of crystallized cellulose I. The two most abundant wood hemicelluloses are xylans and glucomanans, the xylan content being higher in hardwoods than in softwoods (3–8%).[1]

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A useful technique for analyzing the structure of wood is Fourier Transform Infrared Spectroscopy (FTIR). This technique has been used in previous studies to characterize cellulose.[2–5] Sarkanen et al.[6–8] characterized the lignin of different types of woods by UV and IR. Other spectroscopic techniques have been used to study the structural changes undergone by the cellulose and lignin components of wood as a result of different ageing treatments.[9–15]

The aim of this study was to study the main chemical differences between softwoods and hardwoods of Catalonia using FTIR spectroscopy.

MATERIALS AND METHODS

Thirty different wood samples (see Table 1) were obtained from the northern area of Catalonia (Spain). The samples were seasoned before being analyzed.

FTIR Spectroscopy

FTIR spectra were obtained on a Nicolet AVATAR spectrometer with Csl optics. Finely divided samples (9 mg) of the surface material were ground and dispersed in a matrix of KBr (300 mg), and then compressed at 167 MPa to form pellets. All the spectra were recorded at a resolution of 4 cm^{-1} and consisted of 100 co-added scans. Background spectra were obtained using pure KBr.

The methods used for drawing the baselines are indicated in Figure 1. The baseline for the bands at 1595 and 1510 (1505) cm^{-1} was the tangent at the minimum near 1560 cm^{-1} (parallel to the abscissa axis). For the bands at 1335 and 1316 cm^{-1}, a baseline was drawn between the minima at approximately 1400 and 1305 cm^{-1}, and for the bands at 1270 and 1230 cm^{-1} a baseline was drawn between the minima at approximately 1305 and 1200 cm^{-1}.

RESULTS AND DISCUSSION

The spectra obtained for the softwood trees are shown in Figures 1, 2, and 3, whereas the spectra obtained for the hardwood trees are shown in Figures 4, 5, and 6. In order to characterize the samples, two spectral zones were analyzed: 1800–1100 cm^{-1} and 900–800 cm^{-1}.

Spectral Characterization of the Lignin Component in Hardwood and Softwood

Figures 1–6 show the differences in the FTIR spectra for the lignin component in hardwood and softwood. Clear differences in the infrared spectra related to

Table 1. Names of the thirty woods studied

Wood	Common name	Scientific name
1	Evergreen oak	*Quercus ilex*
2	Common ash	*Fraxinus excelsior*
3	Common alder	*Alnus glutinosa*
4	English oak	*Quercus robur*
5	Black poplar	*Populus nigra*
6	London plane	*Platanus hispanica*
7	Smooth leaved elm	*Ulmus minor*
8	Silver birch	*Betula pendula*
9	Wild cherry	*Prunus avium*
10	Walnut	*Juglans regia*
11	Judas tree	*Cercis siliquastrum*
12	Crape myrtle	*Lagerstroemia indica*
13	Nettle	*Celtis australis*
14	Carob	*Ceratonia siliqua*
15	Date palm	*Phoenix dactylifera*
16	Elder	*Sambucus nigra*
17	Scots pine	*Pinus sylvestris*
18	Deodar	*Cedrus deodara*
19	Italian cyprus	*Cupressus sempervirens*
20	Common yew	*Taxus baccata*
21	Aleppo pine	*Pinus halepensis*
22	Colorado spruce	*Picea pungens*
23	Common box	*Buxus sempervirens*
24	Austrian pine	*Pinus nigra*
25	Common juniper	*Juniperus comunis*
26	Spanish fir	*Abies pinsapo*
27	Giant sequoia	*Sequoiadendron giganteum*
28	European larch	*Larix decidua*
29	Japanese cedar	*Cryptomeria japonica*
30	Eastern white pine	*Pinus strobus*

the intensity, shape, and location of some bands were detected: the 1740 cm^{-1} band; the ratio of the 1595 cm^{-1} band to the 1510 cm^{-1} band (in softwoods) and to the 1505 cm^{-1} band (in hardwoods); the ratio between the 1270 and the 1230 cm^{-1} bands; and the location of the bands at 832 cm^{-1} (for hardwoods) and at 869 and 810 cm^{-1} (for softwoods).

The band intensity near 1740 cm^{-1} was greater in hardwoods than in softwoods. This is attributed to the stretching of the free carbonyl groups.[6] Although the carbonyl groups in wood components (cellulose, hemicellulose, and lignin) are mainly in the hemicellulose branched chain component, the intensity of the bands depends on the ratio of holocellulose (cellulose and hemicellulose) content to lignin content in all types of wood. Detailed

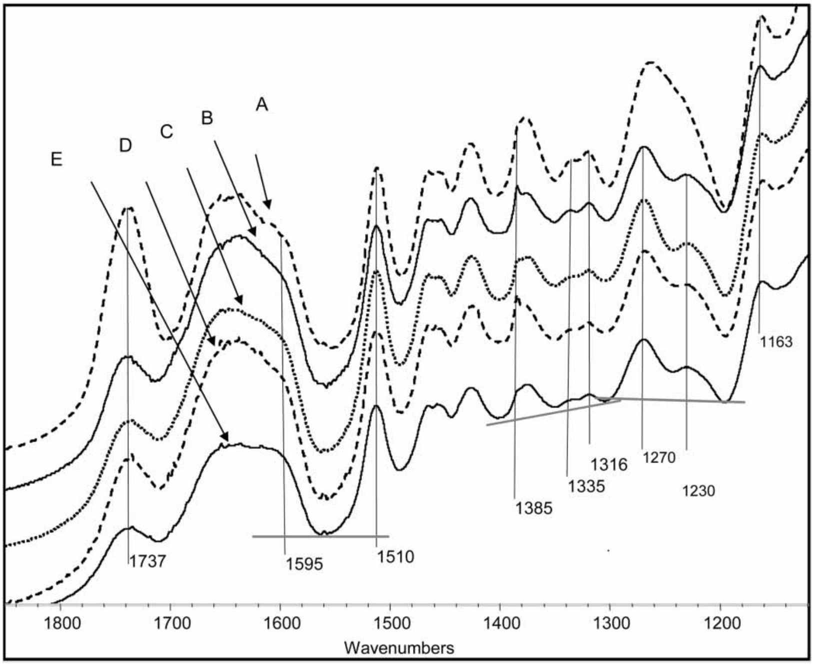

Figure 1. The 1800 to 1100 cm^{-1} region of the infrared spectra for softwood trees (A: *Sambucus nigra*; B: *Pinus sylvestris*; C: *Cedrus deodara*; D: *Cupresus sempervirens*; E: *Taxus baccata*).

information pertaining to the precise values of the components in wood is summarized in different publications.[16] This information shows that, in general, the ratio of holocellulose to lignin is higher in hardwoods than in softwoods, as is corroborated by the band at 1740 cm^{-1}. It should be pointed out, however, that some hardwoods (e.g., *Betula pendula*) have lower intensity bands than some softwoods (e.g., *Sambucus nigra* and *Buxus sempervirens*). One possible interpretation is based on the amount of carbonyl absorption found in the wood components.

The other feature that differed between the hardwoods and softwoods was the precise position of the peak near 1740 cm^{-1}. In a previous study, Owen and Thomas[17] demonstrated that the peak around 1740 cm^{-1} was displaced to lower values in softwoods than in hardwoods. Our results agree with this. As can be seen for the softwoods (Figures 1 and 2) the band is situated at 1737 cm^{-1} whereas it is at 1740 cm^{-1} for the hardwoods (Figures 4 and 5).

Another difference is in the relative intensities of the bands at 1595 cm^{-1} and 1510 cm^{-1} (softwood) or 1505 cm^{-1} (hardwood), which is attributed to aromatic skeletal vibrations.[18] In softwoods, the intensity at

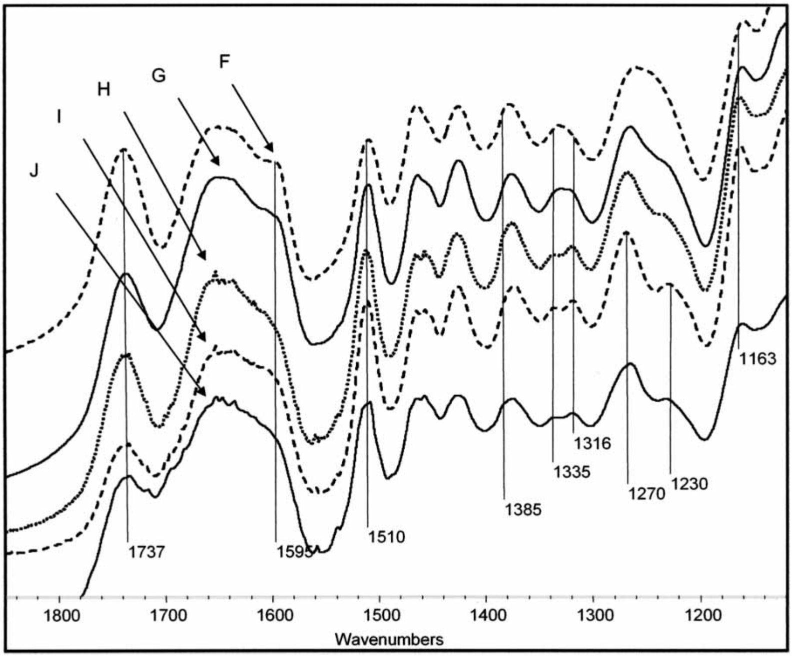

Figure 2. The 1800 to 1100 cm^{-1} region of the infrared spectra for softwood trees (F: *Buxus sempervirens*; G: *Juniperus comunis*; H: *Abies pinsapo*; I: *Sequoiadendron giganteum*; J: *Larix decidua*).

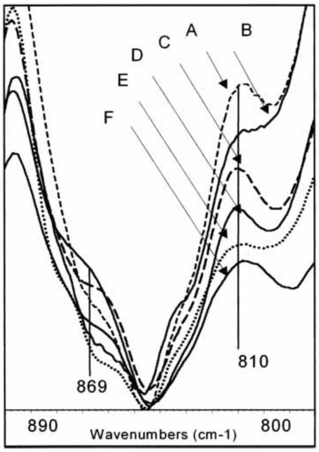

Figure 3. The 900 to 800 cm^{-1} region of the infrared spectra for softwood trees (A: *Sambucus nigra*; B: *Pinus sylvestris*; C: *Cedrus deodara*; D: *Cupresus sempervirens*; E: *Taxus baccata*; F: *Buxus sempervirens*).

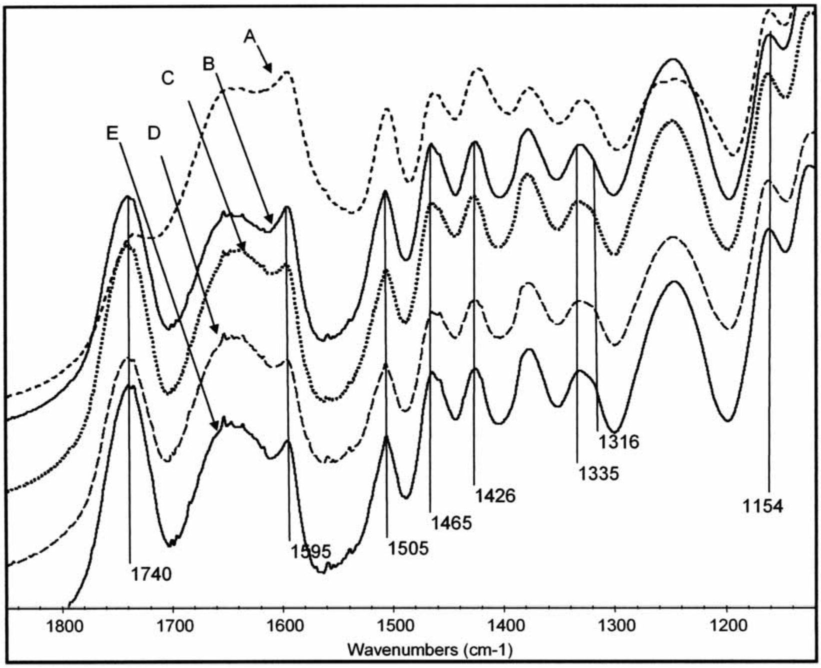

Figure 4. The 1800 to 1100 cm^{-1} region of the infrared spectra for hardwood trees (A: *Betula pendula*; B: *Ulmus minor*; C: *Prunus avium*; D: *Juglans regia*; E: *Platanus hispanica*).

1595 cm^{-1} is less than that of the band at 1510 cm^{-1}, whereas in hardwoods the two bands have similar intensities. Figure 7 shows the results of the ratio 1595/1510, where the values for the hardwood samples are about 1 (0.9–1.4) and for the softwoods every sample shows a value of less than 1 (between 0.8 and 0.5). This difference is due to the structural differences between the kinds of wood. Softwood lignins consist of guaiacyl (trans coniferyl alcohol) nuclei (80%), whereas hardwood lignins consist of a mixture of guaiacyl (40%) and syringyl (synapyl alcohol) nuclei (60%). Sarkanen et al.[6] demonstrated (using patterns of lignin models for guaiacyl and syringyl types) that the band around 1510 cm^{-1} has a stronger guaiacyl element (softwoods) than the contribution from syringyl (hardwoods).

Another important difference between the two kinds of woods can be seen in the intensities at 1270 and 1230 cm^{-1}. Whereas the band at 1270 cm^{-1} is associated with guaiacyl nuclei, that at 1230 cm^{-1} is attributed to a combination of a syringyl nuclei and cellulose deformation. According to Pandey,[18] it is possible to estimate the ratio between the types of lignin components by using the relative intensities of these two bands.

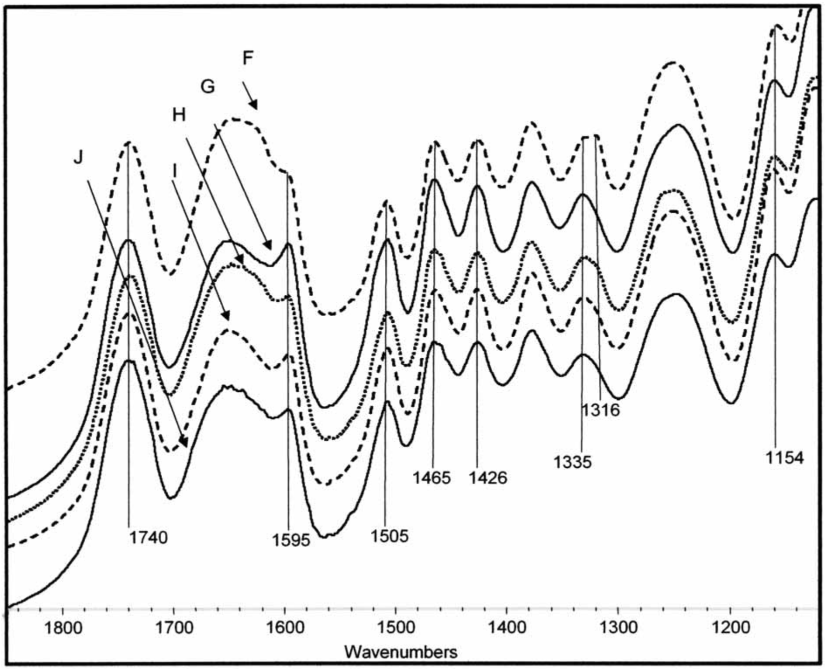

Figure 5. The 1800 to 1100 cm^{-1} region of the infrared spectra for hardwood trees (F: *Populus nigra*; G: *Fraxinus excelsior*; H: *Quercus ilex*; I: *Quercus robus*; J: *Alnus glutinosa*).

In all the hardwoods analyzed, the bands at 1270 and 1230 cm^{-1} appear as a light shoulder, and the main peak appears in an intermediate position near 1252 cm^{-1}. In the softwoods, by contrast, they appear as intense bands and in all the samples the intensity at 1270 cm^{-1} is higher than that at 1230 cm^{-1}. Figure 8 shows that all the hardwood samples have a similar ratio of guaiacyl/syringyl nuclei (1270/1230), which is around 1, whereas in all the softwood samples the guaiacyl nuclei content is higher than the syringyl content [(1270/1230) $>$ 1]. As expected, the results obtained agree with the ratio 1595/1505 (1510).

One of the most important spectral differences between hardwoods and softwoods is in the region located between 800 and 900 cm^{-1}. In softwoods a band appears at 810 cm^{-1}, which is attributed to aromatic C–H out-of-plane deformations of the trisubstituted rings associated with the guaiacyl nuclei. It has a shoulder at 869 cm^{-1}, which is attributed to the same deformation (see Figure 5). However, in hardwoods, an intense band appears at 832 cm^{-1}, which is due to aromatic C–H out-of-plane deformations of the tetrasubstituted rings associated with the syringyl nuclei (see Figure 6).

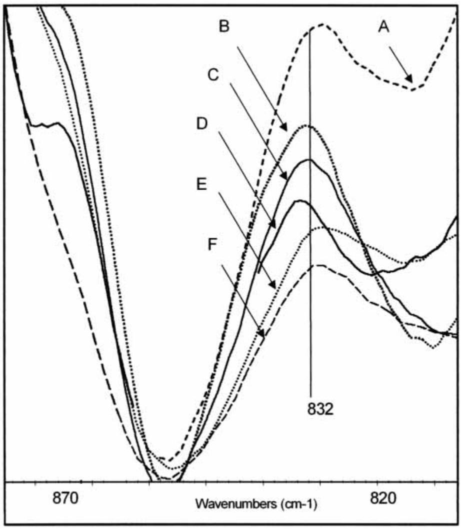

Figure 6. The 900 to 800 cm^{-1} region of the infrared spectra for hardwood trees (A: *Betula pendula*; B: *Ulmus minor*; C: *Prunus avium*; D: *Juglans regia*; E: *Platanus hispanica*; F: *Populus nigra*).

Spectral Characterization of the Cellulose Component in Hardwoods and Softwoods

The most important bands that helped to identify the cellulose component were: 1420 cm^{-1}, attributed to amorphous cellulose and crystallized cellulose II, and 1430 cm^{-1}, attributed to crystallized cellulose I. The

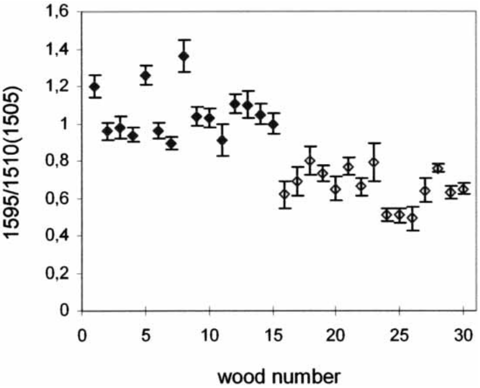

Figure 7. 1595/1510 cm^{-1} ratio as a function of wood type. Hardwood (◆); Softwood (◇).

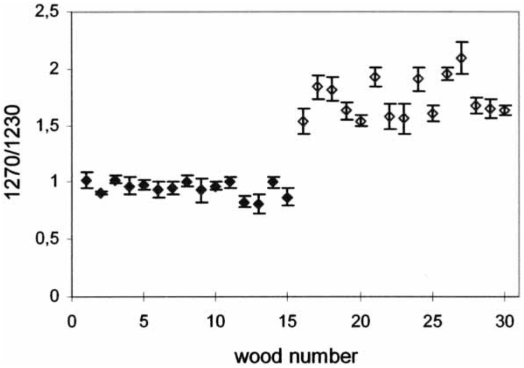

Figure 8. Guaiacyl/syringyl nuclei (1270/1230 cm^{-1}) ratio as a function of wood type. Hardwood (◆); Softwood (◇).

spectra obtained for all the samples showed a band at 1426 cm^{-1}, which indicated that both wood types contained a mixture of crystallized cellulose I and amorphous cellulose.[2,4]

Another important difference in the intensity and shape of the spectra was observed between the different woods: (i) the doublet at 1335 and 1316 cm^{-1}, which mainly appears in cellulose with a high crystalline cellulose I content; and (ii) the location of the bands at 1154 cm^{-1} (hardwood) and 1163 cm^{-1} (softwood). The band at 1154 cm^{-1}, attributed to cellulose C–O–C bridges in hardwoods, is shifted to 1163 cm^{-1} in softwoods (Figures 1–4). In crystallized cellulose this band is located at 1163, whereas for amorphous cellulose it is located at 1155 cm^{-1}.[2]

To determinate the relationship between crystalline cellulose I and amorphous cellulose contents, the ratio between the 1335 and the 1316 cm^{-1} bands, assigned to C–OH in plane bending and CH_2 wagging, respectively, can be used.[3,5] A decrease in the ratio indicates an increase in crystallinity. Figures 1, 2, 4, and 5 show that the band at 1316 cm^{-1} is less intense in hardwoods than in softwoods. Based on this (except in the case of common box, *Buxus sempervirens*), and corroborated by the location of band at 1154 cm^{-1} in hardwoods and shifted to 1163 cm^{-1} in softwoods, it can concluded that the crystallized cellulose content is higher in softwoods than in hardwoods (see Figure 9).

CONCLUSIONS

Clear differences in the degree of absorbance, shape, and location of the bands in the infrared spectra were detected for the hardwoods and softwoods analyzed. It has been shown that it is possible to obtain information about

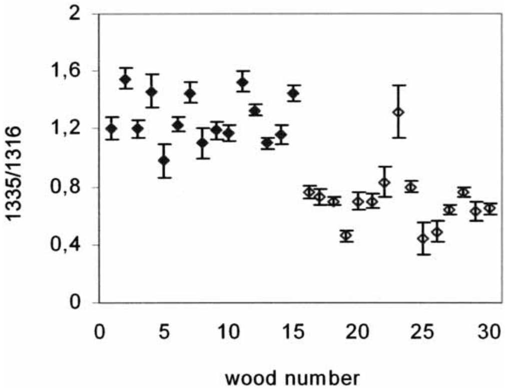

Figure 9. Relationship between amorphous cellulose and crystallised cellulose I content (1335/1316 cm^{-1}) as a function of wood type. Hardwood (◆); Softwood (◇).

the chemical composition and structure of wood components (lignin and holocellulose), mainly by analysis of the fingerprint region between 1800 and 800 cm^{-1}.

The intensity of the band at 1740 cm^{-1} is slightly greater in hardwoods than softwoods, due to the increased amount of acetyl groups in the hemicellulose component in hardwoods. Another significant difference is the relative intensities at 1505, 1425, and 1270 cm^{-1}, which are stronger in softwoods, whereas the bands at 1600, 1465, 1320, and 1220 cm^{-1} are stronger in hardwoods.

Hardwood samples show similar intensities at 1595 and 1510 cm^{-1} due to the predominance of syringyl units, whereas the softwood spectra show higher intensities at 1510 cm^{-1} than at 1595 cm^{-1}, which can be attributed to a higher content of guaiacyl units.

Based on the guaiacyl-syringyl ratio (1270/1230 cm^{-1}), we have been able to show that hardwood lignin is composed of both syringyl and guaiacyl nuclei, whereas softwood lignin is basically composed of guaiacyl nuclei. The 1335/1316 cm^{-1} ratio is related to the contents of crystalline cellulose I and amorphous cellulose, and from the spectroscopic data we can conclude that the cellulose I component is higher in softwoods than in hardwoods.

Although it can be concluded from the results that the thirty samples analyzed can be classified into one of the two known types of wood, hardwood and softwood, we have observed differences in the general behavior of some samples. The most relevant case was the *Buxus sempervirens* sample, due to the high 1335/1316 cm^{-1} ratio and the absorbance value at 1740 cm^{-1}. The reason for the anomalous behavior of *Buxus sempervirens* is not clear to us, but one possibility is that box is not a tree but is really a bush.

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